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54 Microelectronic sensor assembly.

57 A microelectronic semiconductor element 12 is mounted on to a header 13, and integrally combined with one or more metallic sensing electrodes 20, 21 by encapsulation in a chemically and electrically inert material 19, to provide a miniature sensor assembly suitable for the detection and measurement of oxygen and other substances.

Gold or gold alloy semiconductor-device bonding wires are suitable as the metallic sensing electrodes and permit low-cost, mass-production capability. The basic assembly can be engineered in various forms for different biomedical applications and is readily modified, by the addition of appropriate electro-active films to the device surface, into a sensor for a variety of chemical and biochemical substances, including enzyme substrates.

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MICROELECTRONIC SENSOR ASSEMBLYField of the Invention

5 The present invention relates to an active, miniature, solid-state amperometric electrode assembly. In particular, the invention relates to a novel electrode assembly with integral microelectronic signal-processing, which is particularly well suited for
10 application as an oxygen-sensing electrode.

Description of the Prior Art

15 Amperometric electrodes are well known and widely used for the detection and measurement of various chemical properties. ("Chemical properties", as used herein, shall be understood to include ion activity and concentration, presence and concentration of enzymes, substrates, antibodies, antigens,
20 hormones and reducible gases, and the presence, concentration and activity of any of a variety of chemical and biochemical substances including the constituents of enzymatic systems, e.g. serum enzymes, glucose, lactates, pyruvates, creatinine,
25 urea and the constituents of the immunochemical system).

 The most widely used amperometric electrode is that used for measuring the partial pressure of oxygen (pO_2) in aqueous solution, commonly called a pO_2 electrode as originally developed by Clark
30 (Trans. Am. Soc. Art. Int. Organs, 2 (1956), 41-8) which is based on amperometric measurement of oxygen reduced at a cathode maintained at typically -0.6 V with respect to, for example, a silver/silver-chloride

(Ag/AgCl) non-polarised anode. The electrode is usually separated from the sample by an oxygen permeable membrane. (See "The acid-base status of the blood", (4th Ed.) (1974), pp. 175-181, O. Siggaard-Anderson, Alden and Mowbray Ltd., Oxford.). The cathode material must be relatively inert, and the surface area exposed to the sample must be small in order to restrict depletion of oxygen in the sample by the use of the electrode. In practice, this is usually achieved by sealing a fine platinum wire into a glass rod; for example the Radiometer (Copenhagen, Denmark) Type E5046 pO_2 electrode uses a 20 μm diameter platinum wire supported in a glass rod approximately 7 mm diameter and 12 mm in length. Cathodic reduction of oxygen by this electrode generates an output current of approximately 20 pA/mmHg pO_2 at 37°C, equivalent to a signal current of approximately 3 nA at normal atmospheric pO_2 at a polarizing voltage of -0.65 V. Thus, the source impedance of the electrode is $>10^8$ ohms, and requires sophisticated and sensitive electronic instrumentation to perform current-to-voltage conversion and high-to-low impedance conversion in order to drive recording or display devices. The high electrode impedance requires that the cable between the electrode and the instrumentation must be carefully electrically screened with high quality, low-leakage cable and connectors, which add significantly to the bulk of the electrode. Conventional electrodes of this type are labour-intensive, and costly, to manufacture.

Summary of the Invention

The present invention is concerned with the integration of the cathode electrode, or anode-cathode pair, and an appropriate microelectronic signal-processing device into a single unit, an integrated-circuit amperometric sensor (hereinafter referred to as I.C.A.S.) with unique and significant advantages over the present state-of-the-art electrode, especially with regard to biomedical usage. The present invention also describes techniques and materials for the fabrication of such electrodes which are entirely compatible with the present state-of-the-art of integrated circuit packaging.

The invention provides a miniature sensor assembly for the detection and electrochemical measurement of oxygen and/or other chemical properties of the environment to which it is exposed, comprising: a microelectronic semiconductor element (12) or plurality thereof; a metallic sensing electrode (20, 21) or plurality thereof; a substrate (13) for the physical support of the aforementioned and permitting external electrical connections to be made to the said semiconductor element(s) and electrode(s), integrally combined and enclosed, or partially enclosed, in a chemically-resistant electrically inert material (19) in such a way as to expose a portion of one or more of the metallic electrodes to the environment.

Furthermore, the basic conventional amperometric electrode forms the basis of other types of sensor, such as enzymatic-sensitive devices ("Multi-

purpose electrode with different enzyme systems bound to collagen films", Bertrand, C., Coulet, P.R. and Gautheron, D.C., Anal. Chim. Acta (1981), 126, 23-34.); such devices are an important part of the present invention.

There are various ways in which our invention may be physically engineered; we do not exclude any such ways from the scope of the present invention. Two techniques are described herein- after to illustrate different methods of fabrication of I.C.A.S. devices, which provide the most useful functional forms of sensor. The first technique provides sensors which are of similar physical dimensions to their conventional electrode counterparts, and may therefore be used as a direct and superior replacement for the latter, whereas the second technique describes the fabrication of I.C.A.S. devices of such dimensions, and in such a way, that they may be conveniently mounted as catheter-tip devices for in-vivo biomedical application, for example, as foetal scalp pO₂ electrodes.

The nature of the I.C.A.S. devices described herein also permits improvements in other areas of measurement, such as the transcutaneous pO₂ technique (see "Use of transcutaneous oxygen electrodes in intensive therapy", Aldaidy, W., Skeates, S.J., Hill, D.W., Tinker, J., Intensive Care Medicine (1977), 3 (1), 35-9.), which is presently limited by the relatively large surface area of the conventional electrodes employed therein.

The multifold advantages of the present

invention over conventional state-of-the-art
electrode systems are summarised below:

- 1) The small size of I.C.A.S. devices is particularly useful for biomedical applications such as catheter-tip pO_2 sensors and for transcutaneous pO_2 measurements.
- 2) Low-cost fabrication is easily achieved as the materials and techniques used are already widely used in integrated-circuit encapsulation procedures and are inexpensive.
- 3) I.C.A.S. devices are inherently robust as they are solid-state transducers with no fragile components (e.g. glass) used in their construction.
- 4) Mass-production is readily achieved as the fabrication techniques are well-suited to automation; minimal manual involvement is required.
- 5) Multi-function integration is possible; a plurality of I.C.A.S. devices may be incorporated into a single assembly for the simultaneous detection and measurement of more than one chemical property.
- 6) I.C.A.S. devices have low output impedances, typically 60 ohms (as opposed to approximately 2×10^8 ohms) due to the integrated current-to-voltage and impedance conversion

circuitry. This eliminates the requirement for low-leakage screened cable access to the sensor, and is particularly important in foetal scalp pO_2 measurements where the environment contains substantial electrical interference and where physical placement of the sensor is difficult.

- 5
- 10 7) Various ways of engineering I.C.A.S. devices provide sensors physically suited to widely different applications, as described hereinbefore.
- 15 8) The electrical output and power requirements of the present invention are compatible with instrumentation which is presently used with conventional amperometric electrodes.
- 20 9) The sensitivity of I.C.A.S. devices is superior to that of conventional amperometric systems which is limited by three factors: (i) the quality of the electrode surfaces; (ii) the quality of the electronic instrumentation; (iii) the quality of the electrical connections between the two former items (with regard to electrical leakage and adequacy of screening). I.C.A.S. devices eliminate
- 25
- 30 the latter requirement.

In accordance with one aspect of the present invention, the I.C.A.S. device is engineered in such a way that it is dimensionally similar to its conventional

counterpart, and therefore physically compatible with instrumentation already widely established in many analytical laboratories.

In accordance with another aspect of the present invention, the I.C.A.S. device is engineered to form sensors of such a small size and robust nature that they may be mounted on to catheter-tips or adapted to in-vivo biomedical application.

10 Description of the Drawings

The objects and additional features of the present invention will become apparent from the following description taken in conjunction with preferred embodiments with reference to the accompanying drawings, in which:

Fig. 1. shows a schematic diagram of an operational amplifier in current-to-voltage conversion configuration.

Fig. 2. shows an amperometric electrode pair, polarizing voltage source, and current-to-voltage converting amplifier (supra).

Fig. 3. shows an I.C.A.S. device in schematic form, together with associated circuitry.

Fig. 4. shows a partially-completed I.C.A.S. device engineered on a conventional TO-5 type micro-electronic header.

Fig. 5. shows a completed I.C.A.S. device (TO-5 form).

Fig. 6. shows the plan view of a partially-completed I.C.A.S. device mounted

on a flexible printed circuit substrate for catheter-tip type operation.

Fig. 7. shows the end elevation of device of Fig. 6.

Fig. 8. shows the end elevation of device of Fig. 6 after completion of fabrication.

Fig. 9. shows the front elevation of device of Fig. 8.

Fig. 10. shows an I.C.A.S. electrode tip with bare electrodes.

Fig. 11. shows an I.C.A.S. electrode tip with additional films or membranes deposited over the bare electrodes.

Fig. 12. shows an I.C.A.S. engineered into a conventional pO_2 measurement cell.

Fig. 13. shows an I.C.A.S. device engineered as an enzyme-responsive electrode.

Fig. 14. shows an response characteristics of an I.C.A.S. device (T0-5 type).

(For the purposes of clarity, the power supply connections to the amplifiers in Figs. 1 and 2 have been omitted.)

Detailed Description of the Invention

According to the present invention there is provided an amperometric electrode pair and associated semiconductor signal-processing element, or plurality thereof, integrated into a single assembly, and methods for the fabrication of the same using novel techniques.

One or more of the amperometric sensing electrodes may be formed using silver, platinum or other noble metal in wire or strip form; however our technique employs the use of microelectronic bonding wires, such as those commonly used to make electrical connections between the microelectronic signal-processing element and the electrical connections by which external electrical access to it is gained (i.e. the bonding post of a microelectronic mount, such as a TO-5 type header), as one or more of the active sensing electrodes. This is feasible and highly desirable for three reasons:

- 1) bonding wires are commonly made of gold (Au - 1% Si);
- 2) bonding wires are commonly 25 μ m diameter;
- 3) the sensing electrode can be bonded directly on to the microelectronic signal-processing element (or indirectly, via a bonding post).

There are various ways in which the appropriate current-to-voltage and impedance conversion may be effected using, for example, a dual-differential transistor pair or an operational amplifier, as will readily be appreciated by those skilled in the art. The technique and circuit elements described herein-after are chosen as illustrative examples only and not intended to define or impose limitations on the way in which signal-processing is carried out. Rapid progress in microelectronic technology will undoubtedly generate more sophisticated semiconductor elements suitable for this application, and we do not exclude any of these from the scope of the present invention. For descriptive purposes we have chosen to illustrate the principle of operation and mode of fabrication

of I.C.A.S. devices employing an operational amplifier (3) in current-to-voltage conversion mode (Fig. 1) as the signal-processing element, as will be readily appreciated by those skilled in the art, such that the input current I (from current source 1), feedback resistor R (2) and output voltage E_o exhibit the relationship $-E_o = I \times R$. However, the currents generated by amperometric sensing electrodes are small, typically several nanoamperes for $pO_2 = 150$ mmHg, which necessitates the use of an amplifier with a high input impedance. Typically the CA 3140 (R.C.A. Ltd., N.J., U.S.A.) may be used for this purpose. For practical reasons, the use of a 10 megohm feedback resistor (2) provides an output E_o , of 10 mV per 1 nA input current, but this value may be varied in order to increase or reduce sensitivity.

Fig. 2 shows a conventional amperometric electrode pair connected to such circuitry as is described above, and a silver/silver-chloride anode 5, and an inert metallic (gold) cathode 6 exposed to a conducting aqueous solution 7 in a container 8, polarized by a variable voltage source 4, set to $\approx +0.65$ v with respect to system common and hence with respect to the cathode which is connected to the amplifier virtual earth port. The current generated by the reduction of oxygen at the cathode 6 provides a proportional output voltage E_o at low impedance (60 ohms) suitable for driving peripheral recording and/or display instrumentation.

The present invention (Fig. 3) comprises an assembly with sensing electrodes (5,6) and signal-processing element (3) integrated and encapsulated into a single element (11), with electrical access to a

polarizing voltage source (4), a power supply (9,10) and a gain-determining resistor (2). The physical implementation of such a device is described below; first, in T0-5 format; second, in "catheter -tip" format.

I.C.A.S. fabrication I: T0-5 format

(1) The integrated-circuit amplifier (Fig. 4) 12 is mounted on to a T0-5, or similar, micro-electronic header 13. The chip is electrically connected to the header bonding posts 15 using well-known wire bonding techniques employing fine gauge (25 μ m) gold wire 14.

(2) The header-chip wire bond to the inverting input of the amplifier is made 16 and the wire is not cut but pulled vertically upwards before being severed. (Alternatively, a separate bond to either the chip bonding pad or the header bonding post may be made and the wire drawn upwards as before). This provides a loose 25 μ m diameter gold wire 17 bonded directly on, or indirectly to, the inverting input of the amplifier 12.

(3) A counter electrode (e.g. an anode) is formed by bonding another gold bonding wire on to an unused header post, in a similar fashion, or by using a larger diameter silver wire 18, electrically connected, and bonded to, a spare post.

(4) An encapsulating agent is used to enclose all of the electrical connections on the surface of the header (Fig. 5). There are several agents suitable for this purpose. The general requirements are that the material must be a good electrical insulator, must be resistant to chemical attack, solvation and ionic penetration, must adhere well to the header surface, must have a viscosity low enough to flow around the

delicate bonding wires without damaging them or the flying leadouts (17,18), and must be applicable using methods which are compatible with mass-fabrication processes. We have found that a slightly thixotropic epoxy is suitable, such as Epo-Tek H54 (Alpha Metals Ltd., Surrey, England), which may contain 1.8% Azo black dye as an optical mask (Alpha Metals Ltd.), but we have already described the use of a superior encapsulating agent, Bis-GMA (and Bis-GMA urethane adducts) in an earlier U.K. patent application (No. 8111199) for a similar purpose. Bis-GMA (an adduct for bis-phenol A and glycidyl methacrylate [2,2-bis(p-(2-hydroxy 3-methacryloxy propoxy)phenyl)propane] is a photopolymerizable plastic used in the dental profession for sealing occlusal surfaces for the prevention of dental caries.

Several drops of Bis-GMA resin are applied to the surface of the header and flow over and around the bonding wires and the chip, forming a dome of fluid material 19. This is polymerized by brief (30-120 s) exposure to U.V. radiation, and the excess surface material is ultrasonically rinsed off (10 s) in isopropyl alcohol, or similar solvent.

(5) The sensing electrodes (20,21) are machined and polished flush with the surface of the encapsulating material.

I.C.A.S. fabrication II: catheter-tip format

(1) The operational amplifier element 22 (Figs. 6 to 9) is affixed with cyanoacrylate adhesive to the tip of a flexible printed circuit (FPC) strip comprising an array of copper strips 24 on a flexible plastic substrate 23 which is terminated with a suitable connector for electrical access. The amplifier is appropriately wire-bonded 25 to the conducting strips.

(2) A silver plate 26 approximately 1 mm x 2 mm x 0.2 mm is affixed to the tip of the FPC with cyanoacrylate adhesive.

5 (3) A wire bond 27 is formed between the proximal edge (i.e. chip side) of silver plate 26 and a conductive strip on the FPC.

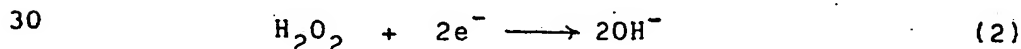
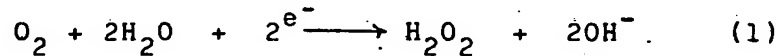
(4) A gold wire bond 28 is made between the distal edge of silver plate 26 and the inverting input of the amplifier chip 22.

10 (5) The tip of the FPC is dip-coated in encapsulating material 29 (vide supra) which is polymerized as appropriate to the material.

(6) The tip of the assembly is machined away and polished, (Fig. 8), such that a gold bonding
15 wire connected to the amplifier inverting input is exposed 28 and also disconnected from the silver plate 26 to which it was bonded for the purpose of simple fabrication.

(7) The assembly is mounted into a
20 catheter-tip, if so required, for biomedical usage.

It must be noted that, in the descriptions hereinbefore, the terms "anode" and "cathode" are interchangeable, since, for the detection of oxygen, a positive polarizing voltage is required, whereas
25 a negative polarizing potential is required for the detection of hydrogen peroxide in accordance with the electrode reactions:



The materials used for the anode and cathode may be selected according to the type of application required of the I.C.A.S. device, but the
35 most common requirement is that the cathode (connected

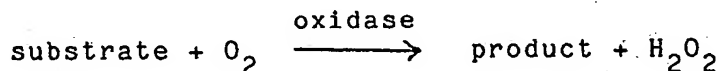
to amplifier inverting input) is gold, and that the anode is silver, subsequently electrolytically chloridised by well-known techniques to form a non-polarizable (i.e. reversible) silver/silver-chloride electrode. While we advocate a gold cathode and silver/silver-chloride anode, we do not rule out the use of other materials in this context, or of a remotely situated, i.e. non-integral, anode. For example, a stainless steel hypodermic needle has been used as the anode in a gold-cathode oxygen electrode (see "A hypodermic needle pO_2 electrode", Wahlen, W.J. and Spande, J.I., J. Appl. Physiol. (1980), 48, 186-7).

The active, chemical-sensing surface of the I.C.A.S. device is shown in simplified form in Fig. 10, and comprises typically a silver anode 22 with chloridised, exposed tip 23 and a gold cathode 24 contained in chemically-resistant encapsulation 26. The use of bare electrodes of this type in blood analysis may sometimes initiate protein deposition on the electrode surfaces. Fig. 11 shows an improved system for biomedical application incorporating a thin film of phosphate buffer in agarose gel form 27 and a gas permeable membrane 28 affixed to the device surface by dip-coating, or other means, so that the electrode system is partitioned from the blood sample under test. The membrane may be made from polypropylene, polyethylene, teflon or similar material such as is used in conventional electrode systems, and having a typical thickness of 20 μm .

I.C.A.S. devices may be used in conventional electrode assemblies to act as superior replacements for the active conventional elements (e.g. platinum in glass) as shown in Fig. 12, where a device, as

described in Fig. 10, is mounted into a holster 32 containing a phosphate buffer 29 and having a gas-permeable membrane 30 located over the I.C.A.S with a rubber or silastic O-ring 33. A remote silver/silver-chloride anode 31 may be used if already present in a conventional electrode holster.

A further important application of I.C.A.S. devices is their use as enzymatic-responsive sensors, when appropriately modified (Fig. 13). This involves the attachment of one or more suitable membranes 34,35 to the surface of a bare I.C.A.S., by dip-coating, physically locating or other means, and polarizing the secondary electrode (i.e. not the electrode connected directly to the integral amplifier) at approximately -650 mV such that the device acts as a hydrogen peroxide sensor and generates a signal in proportion to the amount of hydrogen peroxide oxidised at the primary electrode. The membrane or membranes may be polymer coatings of immobilized enzyme, such that an enzymatic reaction, with or without appropriate co-factors, which liberates hydrogen peroxide:-



can be sensed by the I.C.A.S. device. Typically, glucose oxidase can be used for glucose, and lactate dehydrogenase for lactate. Modifications of this type with respect to conventional amperometric electrodes have already been referred to (Bertrand et al., supra).

Fig.14 shows the response characteristics of an I.C.A.S. fabricated according to the methods described above (I.C.A.S. fabrication I: T0-5 format), using Bis-GMA encapsulant polymerized with U.V. light

for 120 seconds, and employing a CA 3140 amplifier with
10 megohm element feedback resistor, a 25 μm diameter
Au-1% Si bond-wire cathode, and a 0.7 mm x 0.3 mm
silver anode, surface-chloridised in 0.1 mol dm^{-3} HCl
at 50 μA for 5 seconds.

The device was mounted on the tip of a
polycarbonate tube, forming a dip-type sensor, and
supported in 25 ml 0.2 mol dm^{-3} KCl solution at 24°C.
An oxygen/nitrogen gas stream was bubbled through the
solution from a Wosthoff pumping system, set
initially to deliver 0% O_2 ; 100% N_2 , and a current-
voltage curve was obtained (Fig. 14, curve A) by
sweeping the anode potential from 0 V to +1.1 V in
10 mV increments (2s/increment) under minicomputer
control (HP 9815). The oxygen percentage in the gas
mixture was incremented by 10% and after the system
had equilibrated, a second current-voltage curve was
obtained (Fig. 14, curve B). This process was
repeated up to a 50% oxygen level (Fig. 14, curve
F), allowing a set of curves to be obtained.

CLAIMS:

1. A miniature sensor assembly for the detection and electrochemical measurement of oxygen and/or other chemical properties of the environment to which it is exposed, comprising: a microelectronic semiconductor element (12) or plurality thereof; a metallic sensing electrode (20, 21) or plurality thereof; a substrate (13) for the physical support of the aforementioned and permitting external electrical connections to be made to the said semiconductor element(s) and electrode(s), integrally combined and enclosed, or partially enclosed, in a chemically-resistant electrically inert material (19) in such a way as to expose a portion of one or more of the metallic electrodes to the environment.

2. A miniature sensor assembly according to claim 1, where one or more of the electrodes is a gold or gold-alloy microelectronic bonding wire, a wire of platinum, or other noble metal, or a silver wire, strip or plate.

3. A miniature sensor assembly according to claim 1 or 2, where the microelectronic semiconductor element is an operational amplifier or a dual-differential transistor pair.

4. A miniature sensor assembly according to any of claims 1 to 3, where the encapsulation material is Bis-GMA or a Bis-GMA urethane adduct, polymerized by U.V. irradiation or other appropriate means.

5. A miniature sensor assembly according to any of claims 1 to 4, where the substrate is a microelectronic header, including TO-5, TO-99, CERDIP and DIL types, a flexible or non-flexible printed-circuit element, or is formed on a ceramic or similar base using thick-film techniques.

6. A miniature sensor assembly according to any of claims 1 to 5, where one or more of the exposed metallic electrodes is overlain by a liquid or gel film containing an electrolyte or buffered electrolyte, overlain by a thin, gas-permeable or selectively gas-permeable membrane of polypropylene, teflon, polyester or similar material.

7. A miniature sensor assembly according to any of claims 1 to 6, where one or more of the exposed metallic surfaces are collectively or individually overlain by one or more membranes containing, or having bound thereto, specifically reactive enzyme system.

8. A miniature sensor assembly according to any of claims 1 to 7, affixed to a catheter tip for biomedical use.

9. An instrument or apparatus including a miniature sensor assembly according to any of claims 1 to 7.

10. A miniature sensor assembly according to any of claims 1 to 7, engineered into a flow-through cuvette or into a transcutaneous, gas-sensing electrode.

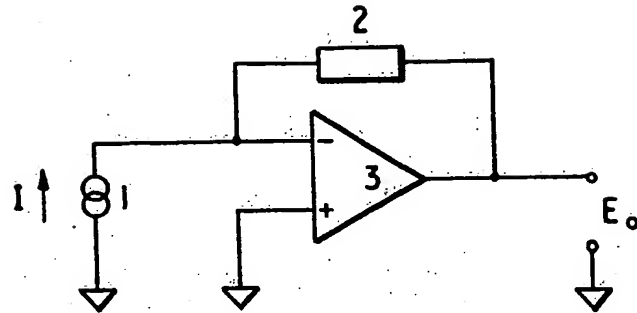


FIG. 1.

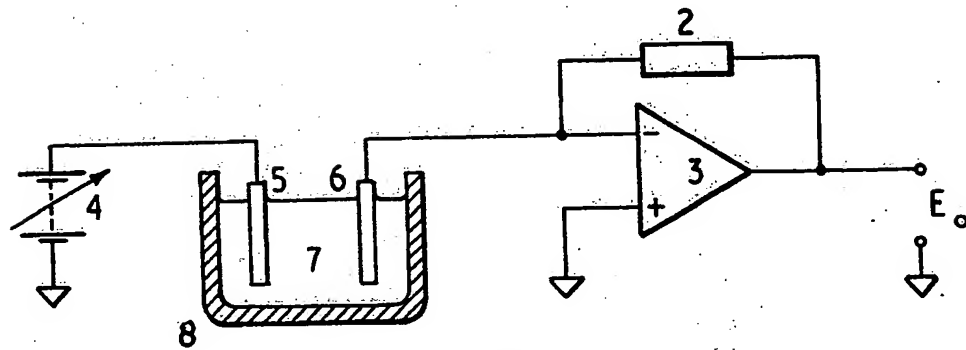


FIG. 2.

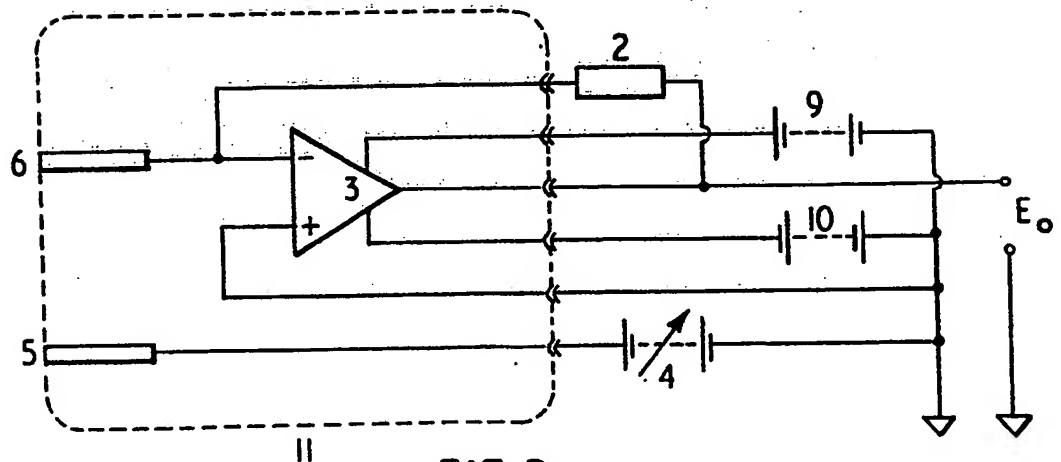


FIG. 3.

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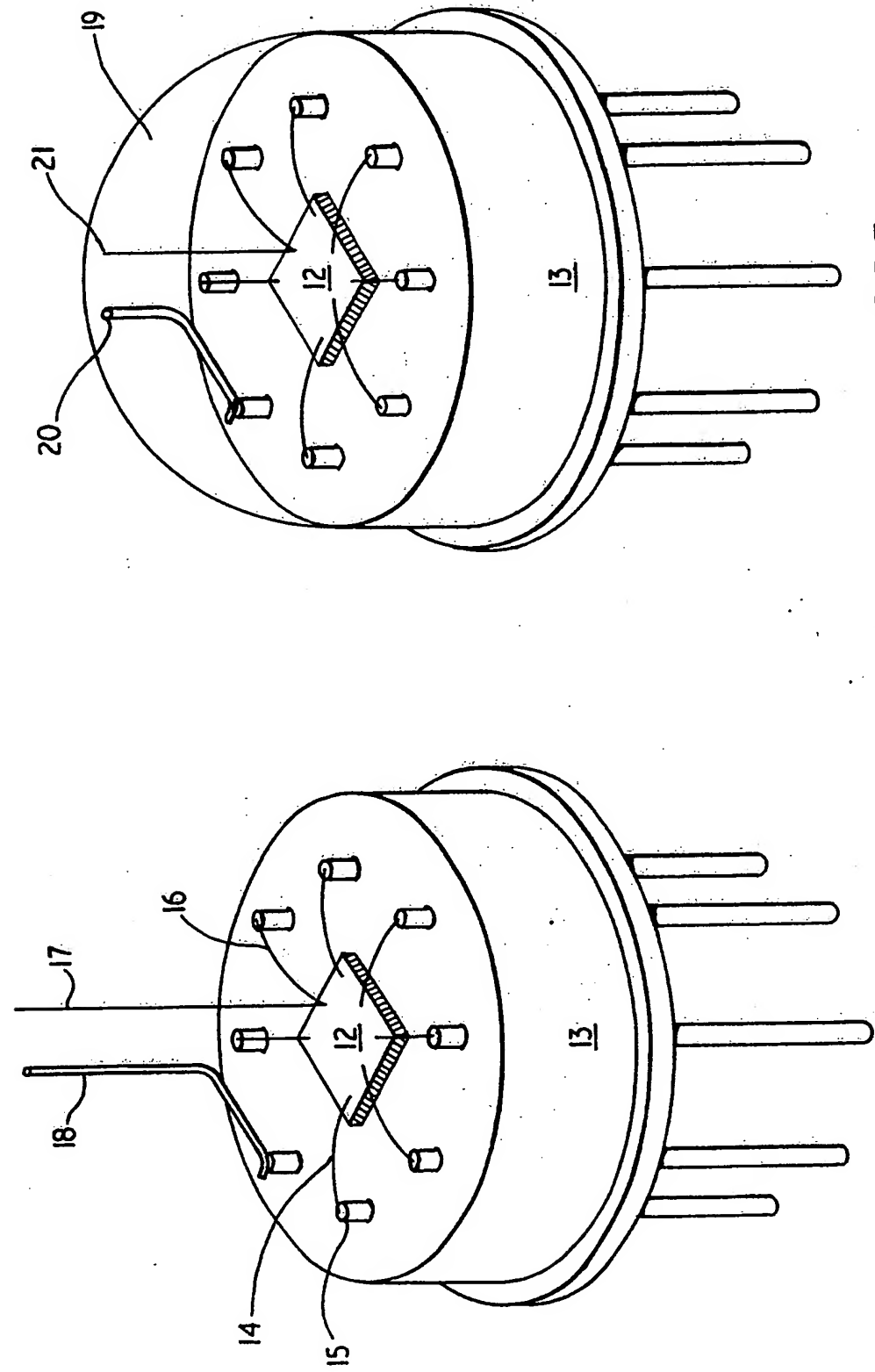
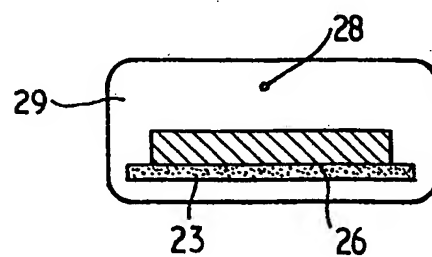
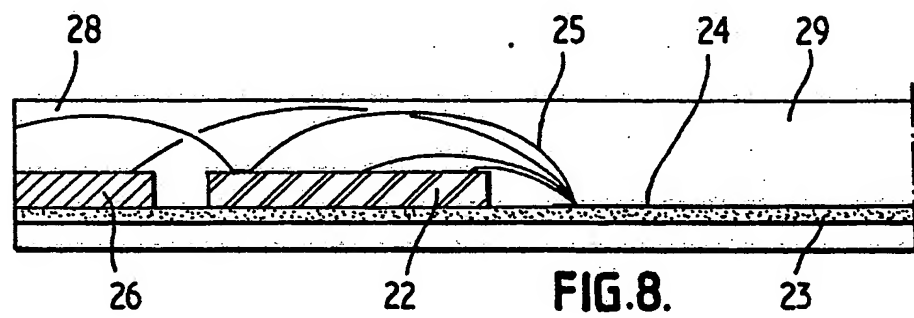
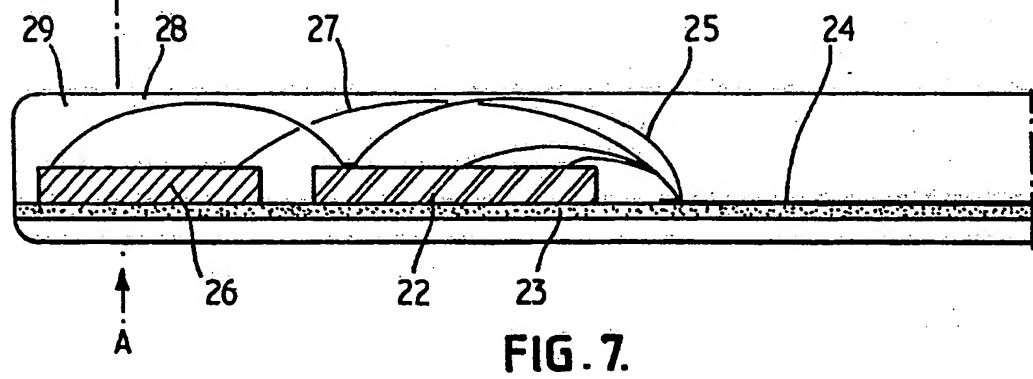
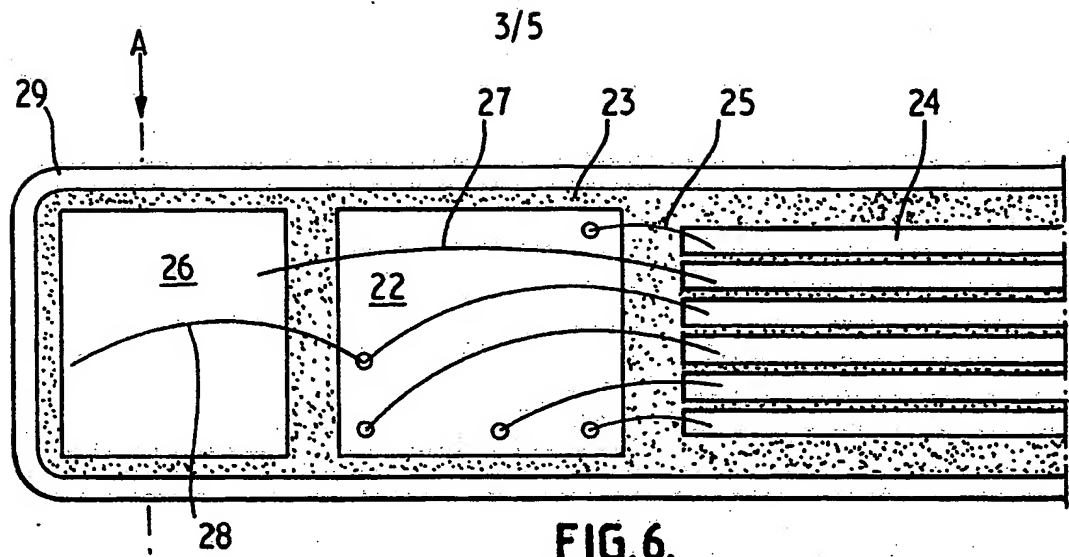


FIG. 5.

FIG. 4.



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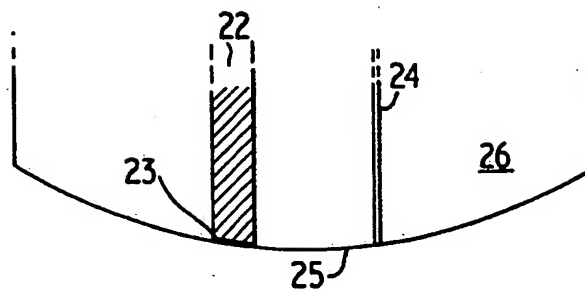


FIG. 10.

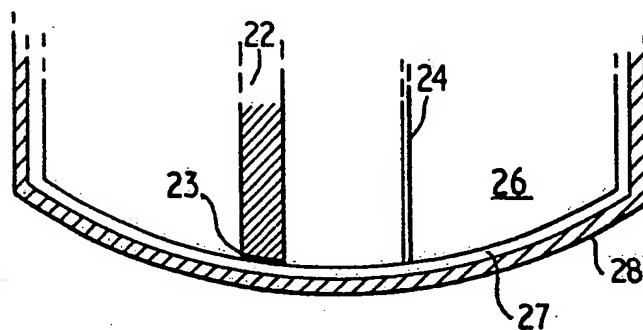


FIG. 11.

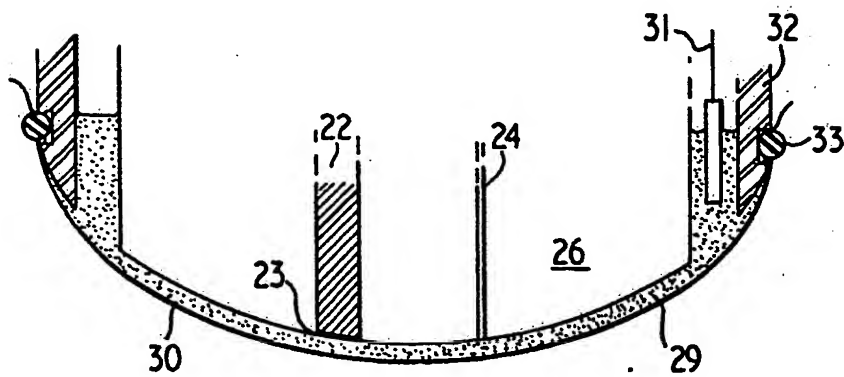


FIG. 12.

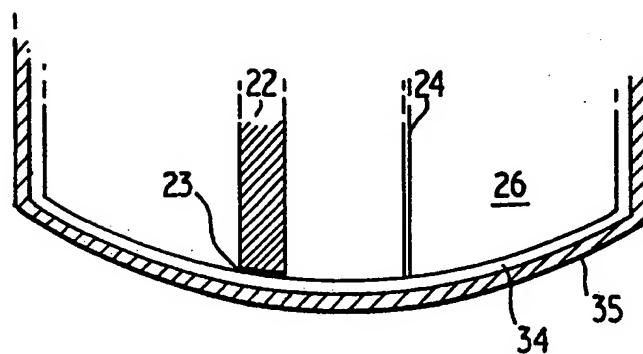
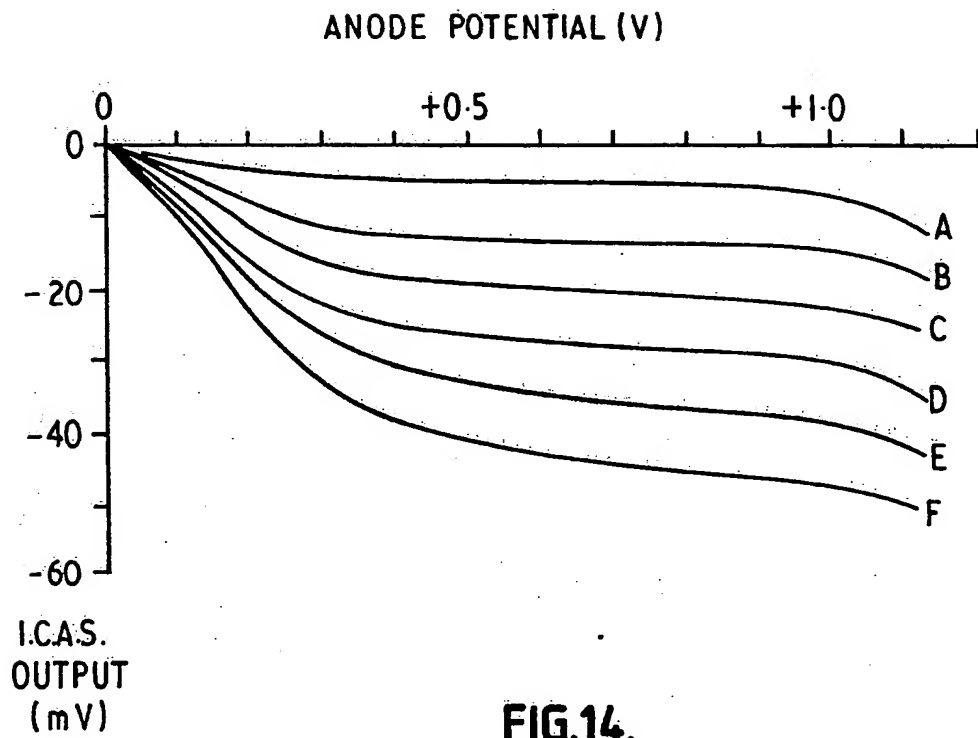


FIG. 13.

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European Patent
Office

EUROPEAN SEARCH REPORT

0078590

Application number

EP 82 30 1868.4

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	<p>EP - A1 - 0 012 035 (TECHNICON INSTRUMENTS CORP.)</p> <p>* page 3, lines 13 to 35; pages 4 to 12 *</p> <p>---</p>	1-10	<p>G 01 N 27/30</p> <p>A 61 B 5/14</p>
A	<p>GB - A - 1 587 880 (B. HAGIHARA)</p> <p>* pages 2, 3 *</p> <p>---</p>	1,2, 6-8	
A	<p>DE - A1 - 2 548 406 (GENERAL ELECTRIC CO.)</p> <p>* pages 3, 4, 6 *</p> <p>& US - A - 3 900 382</p> <p>---</p>	1,2,6, 7	<p>TECHNICAL FIELDS SEARCHED (Int.Cl. 7)</p>
A	<p>DE - A1 - 2 906 201 (N.V. PHILIPS' GLOEI-LAMPENFABRIEKEN)</p> <p>* pages 3, 8 to 10 *</p> <p>& GB - A - 2 014 739</p> <p>---</p>	1,3, 6-10	<p>A 61 B 5/00</p> <p>G 01 N 27/00</p> <p>H 01 L 21/00</p>
A	<p>DD - A - 148 988 (D. RAHNER et al.)</p> <p>* pages 2, 3 *</p> <p>---</p>	1,2, 6,7	
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<p>X The present search report has been drawn up for all claims</p>			
Place of search Berlin		Date of completion of the search 29-06-1982	Examiner DIETRICH

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